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The collective dynamics of liquid deuterium fluoride are studied by means of high-resolution quasielastic and inelastic neutron scattering over a range of four decades in energy transfer. The spectra show a low-energy coherent quasielastic component which arises from correlated stochastic motions as well as a broad inelastic feature originating from overdamped density oscillations. While these results are at variance with previous works which report on the presence of propagating collective modes, they are fully consistent with neutron diffraction, nuclear magnetic resonance, and infrared/Raman experiments on this prototypical hydrogen-bonded fluid. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2743021]

I. INTRODUCTION

Hydrogen fluoride (HF) is the molecule with the strongest as well as the simplest hydrogen bond in nature, and thus it constitutes an important benchmark to understand the behavior of more complex hydrogen-bonded liquids such as water. The stringent conditions posed by the handling and containment of this highly corrosive material have largely prevented experimental access to many of its properties and, therefore, comprehensive experimental investigation of its structure and dynamics has only become possible in the past few years. In fact, structural reports on liquid HF are scarce, and only recently its structure at the pair correlation function level has been reported.[1] The structure of HF in the solid is also known from crystallographic studies at low temperatures. At $T=4$ K and ambient pressure, HF crystallizes in the orthorhombic space group $Cmc2_1$ where the structure is comprised of parallel zigzag chains along the b axis.[2] Each molecule binds to its two nearest neighbors through hydrogen bonds and the lattice structure is further stabilized by interchain van der Waals interactions, believed to be between one and two orders of magnitude weaker than the bonds holding the chains together. Contrary to other hydrogen halides, the crystal structure described earlier is retained in the solid at all explored temperatures. Even more surprisingly, the F···F distance ($r_{FF}=2.5$ Å) is only 0.03 Å shorter than its gas-phase value. Knowledge of its static correlations within the liquid has emerged from recent studies employing a combination of neutron and high-energy x-ray diffraction.[1] It is generally accepted that the static structure of liquid HF is composed of finite hydrogen-bonded chains showing a low degree of branching. However, little is known about tear and repair processes for the intermolecular hydrogen bonds or, specifically, about the residence time of a molecule within a hydrogen-bonded state.

Studies concerning the dynamics in the crystalline solid state have mostly been performed using optical methods[3] and date as far back as the pioneering lattice-dynamics studies of Axmann *et al.*[4] Within the liquid state, dynamical properties were explored some time ago via inelastic neutron scattering,[5] but limitations in energy resolution did not allow for an unambiguous determination of transport coefficients. Later, Ring[6] analyzed the inelastic neutron scattering of liquid and solid HF by considering the vibrational modes of hydrogen-bonded chains. This author concluded that the features found in the spectra could not be accounted for by considering the chain modes alone; therefore, there must be some other motion or structural feature that is responsible for the remaining scattering. More recent reports using inelastic x-ray scattering with a resolution in energy transfers of 1.6 meV have been analyzed by assuming that all the spectral intensity below some 20 meV arises from a single "acoustic mode" with a high-frequency phase velocity asymptotically approaching twice the hydrodynamic value.[7] Finally, indirect inferences about the presence of short-lived polymeric clusters in the liquid have been derived from analysis of optical spectra.[8] Infrared and Raman data at room temperature are consistent with the presence of chains with $n=6-7$ mol-

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ecules having an angle of 42 deg with the average chain axis. At temperatures just above solidification, the chains become marginally longer ($n \approx 8$) with an average angle of 34 deg.[9] Molecular dynamics simulations have also provided a wealth of calculated properties which are quite sensitive to the details of the underlying potential energy landscape.[10] This simulation work depicts the microscopic dynamics within the liquid as being substantially more intricate than that exhibited by simpler liquids such as the liquid alkali metals,[11] where all of the observed intensity can be attributed to collective density oscillations. In fact, detailed analysis of the frequency spectrum[12] reveals well-defined features not accountable for in terms of acousticlike excitations.

Our recent inelastic neutron scattering studies on the dynamics of this material have focused on the high-energy librational and collective opticlike behavior in liquid deuterium fluoride (DF).[13] Low-frequency single-particle motions in liquid HF have also been investigated in a recent incoherent quasielastic neutron scattering study.[14] The aim of the present work is to explore the regime intermediate between the earlier two frequency limits. Specifically, here we provide a detailed survey of the interplay between molecular translations and center-of-mass motions as probed by coherent neutron scattering. In contrast with previous x-ray results[7] (which mostly sample motions of the heavier F atom), the coherent neutron scattering cross section of DF comprises individual nuclear scattering cross sections of comparable magnitude—F (4.017 barn) and D (5.592 barn). This feature enables the study of the spectral response arising from correlated orientational motions, known to contribute significantly to the frequency spectrum.[12] In pursuing such an endeavor, it has become apparent that liquid hydrogen fluoride is not only a remarkable fluid in its own right but also displays a complex hierarchy of dynamical processes spanning several decades in time. These processes may be disentangled via the exploitation of differences in H/D neutron scattering cross sections, as well as by a fine tuning of spectral resolution down to the micro-electron-volt (μeV) range, a task only achievable via a judicious combination of inelastic neutron instrumentation.

II. EXPERIMENTS

Experiments were performed using the IRIS (Ref. 15) and MARI (Ref. 16) inelastic neutron spectrometers at the ISIS Pulsed Neutron and Muon Source, United Kingdom. IRIS enables access to relatively narrow energy ranges with high resolution [$-200-1000$ μeV, $\Delta E = 17.5$ μeV full width at half maximum (FWHM)], whereas MARI was used to perform measurements over wider energy-momentum-transfer ranges by use of higher incident neutron energies. On MARI, two incident energies $E_0 = 14$ and 40 meV were employed to map the dynamic structure factor $S(Q,\omega)$ for momentum transfers up to 4 Å^{-1} and energy transfers up to about 20 meV. The achieved resolutions in energy transfer were $\Delta E = 0.3$ and 0.76 meV (FWHM), respectively. The combination of MARI and IRIS provided a stringent cross-check to ensure that the separation of quasielastic components was not affected by the finite extent of the instrumental energy windows. In both experiments, the spectra were corrected for detector efficiency using a vanadium standard, followed by subtraction of the contribution from the empty cell. Empty-cell spectra were measured at all temperatures investigated.

It cannot be overemphasized that sample preparation is critical in these experiments and, consequently, substantial effort was placed on ensuring the absence of contaminants and impurities in our samples. To this effect, a 20 g sample of DF (Fluorochem, UK) was cryogenically distilled into a 316 stainless steel Swagelok sample cylinder equipped with a needle valve. DF was transferred onto 10 g of K_2NiF_6 in order to remove any aqueous contamination before being transferred into the sample cell. A 5 g sample of anhydrous DF was loaded into an annular geometry sample cell manufactured from monel (Alloy 400) which had previously been surface passivated under an atmosphere of fluorine.[17] An annular geometry of 1 mm was used to minimize absorption and multiple scattering effects. The sample was cooled using a closed-cycle He refrigerator. Spectra were also collected across the melting point ($T = 170-205$ K). The observation of a sharp and distinct drop in elastic-line intensity above $T = 190 \pm 1$ K corresponding to the appearance of a liquid phase provided an upper limit for the presence of H_2O of $<0.5\%$ mol.[18]

Once corrected for background and other instrumental effects, measured intensities were mapped onto a $Q-\omega$ grid. Images were then reconstructed from measured data by means of a recently described purpose-built algorithm[19] which avoids introducing substantial correlation between adjacent bins.

III. RESULTS

A. Quasielastic scattering

DF is mostly a coherent scatterer with a total neutron scattering cross section $\sigma_{\text{scatt}} = 11.67$ barn, of which incoherent scattering amounts to a modest $\sigma_{\text{inc}} = 2.06$ barn. The quasielastic neutron scattering spectrum accessible to IRIS contains a narrow incoherent component at wave vectors well below the maximum in the static structure factor $S(Q)$, $Q_p \approx 1.92$ Å^{-1}, as well as coherent contributions at higher Q. Both single-particle and collective dynamical properties are therefore accessible in a single measurement. The former contributes to the incoherent scattering cross section whereas the latter yields purely coherent scattering with a cross section of $\sigma_c = 9.61$ barn per molecule. The scattered intensity $I(Q,\omega)$ in the quasielastic region may then be decomposed into a sum of incoherent and coherent contributions $L_\alpha(Q,\omega)$,

$$I(Q,\omega) = A\left[\frac{\sigma_{\text{inc}}}{\sigma_{\text{scatt}}} L_{\text{inc}}(Q,\omega) + \frac{\sigma_c}{\sigma_{\text{scatt}}} L_c(Q,\omega)\right] \otimes R(Q,\omega), \quad (1)$$

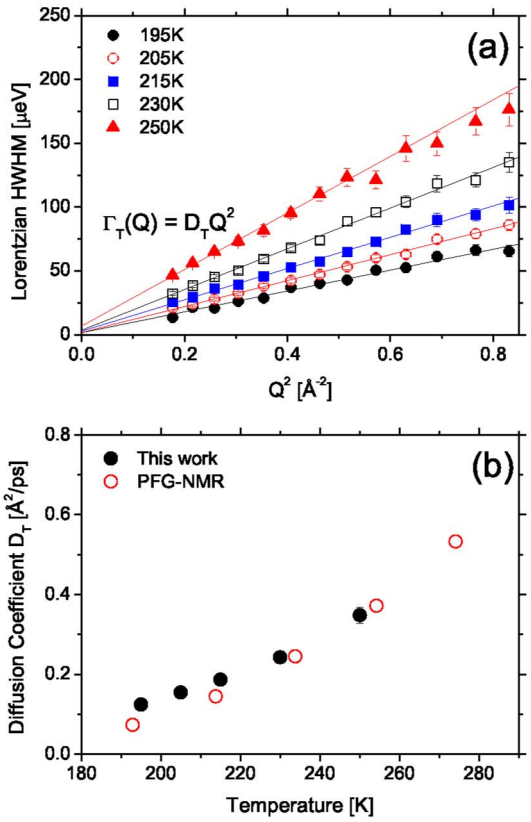

FIG. 1. (Color online) (a) Quasielastic energy widths vs Q^2 measured on IRIS. (b) Comparison between quasielastic (this work) and PFG-NMR (Ref. 18) translational self-diffusion coefficients.

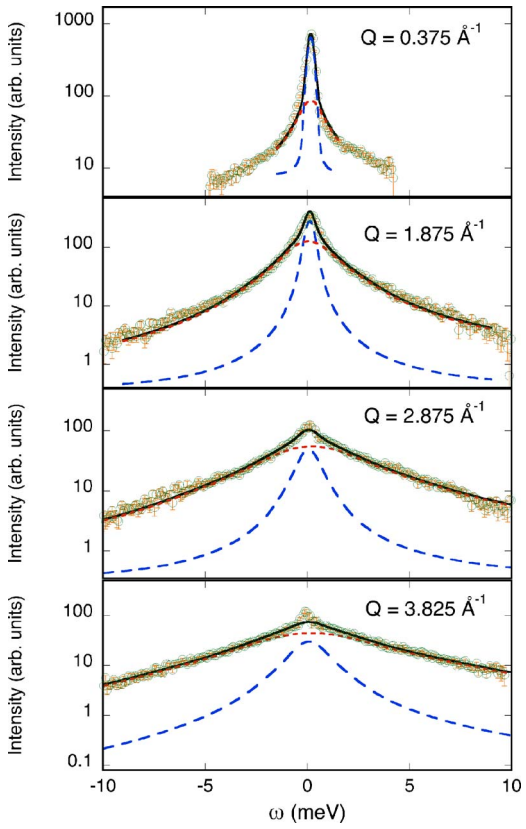

FIG. 2. (Color online) DF neutron spectra as a function of momentum transfer measured on MARI at $T=203$ K and $E_0=14$ meV. Model fits are shown in black and individual Lorentzian components in dashed blue and red.

$$L_\alpha(Q,\omega) = \frac{1}{\pi}\frac{\Delta\omega_\alpha}{\omega^2 + \Delta\omega_\alpha^2}, \tag{2}$$

where A is a global normalization constant and $R(Q,\omega)$ stands for the instrument response. The functional form assumed for both components corresponds to a Lorentzian line shape characterized by a half width at half maximum $\Delta\omega_\alpha$. As we will show later, a separation of coherent and incoherent contributions by purely experimental means is made possible by the rather disparate values exhibited by both incoherent and coherent scattering linewidths. At momentum transfers well below Q_p, scattering is dominated by the incoherent cross section since the static structure factor $S(Q)$ attains modest values. In this limit, incoherent linewidths should follow the behavior expected for hydrodynamic (Fickian) mass diffusion, that is, $\Delta\omega_{\text{inc}}=D_T Q^2$, where D_T stands for a translational (self-) diffusion coefficient.

The wave vector dependence of $\Delta\omega_{\text{inc}}$ as a function of temperature is depicted in Fig. 1(a). To the best of our knowledge, these data represent the first radiation-scattering measurements that provide direct access to the Fickian mass-diffusion limit in liquid DF. The availability of neutron instrumentation with an energy resolution well within the μeV range was essential to achieve this goal. As shown later, knowledge of the neutron scattering response at small energy transfers and its separation into coherent and incoherent contributions is an essential ingredient of the analysis procedure advocated in the present study, as they serve to constrain and interpret neutron data at higher energy transfers. From these low-energy data, translational self-diffusion coefficients D_T may be readily obtained from the slope of $\Delta\omega_{\text{inc}}$ versus Q^2. Our values of D_T are shown in Fig. 1(b). They compare favorably against those obtained via pulsed-field-gradient nuclear magnetic resonance (PFG-NMR),[18] particularly if it is noted that PFG-NMR values are known to be reliable to within 5%–10% (see Izvekov and Voth in Ref. 10). The present results are also in very good agreement with those obtained for liquid HF (Ref. 14) and thus provide a new benchmark for the temperature dependence of this transport coefficient. Contrary to what has been observed for liquid HF,[14] our present results on DF could be fully accounted for via the inclusion of a single Lorentzian component plus a flat background of considerable intensity. This background term signals the existence of faster dynamical processes beyond the maximum energy transfers probed by our highest-resolution measurements. Within the energy range accessible on IRIS, we find no evidence for the presence of a distinct rotational component, as observed in our previous incoherent neutron scattering study.[14]

To fully resolve the aforementioned background term, we have conducted further measurements using the MARI spectrometer at an incident energy of 14 meV. Representative spectra are shown in Fig. 2 and reveal the presence of a second quasielastic component far broader than the MARI resolution function. To provide reliable estimates of such linewidths, we have decomposed the spectra into a sum of

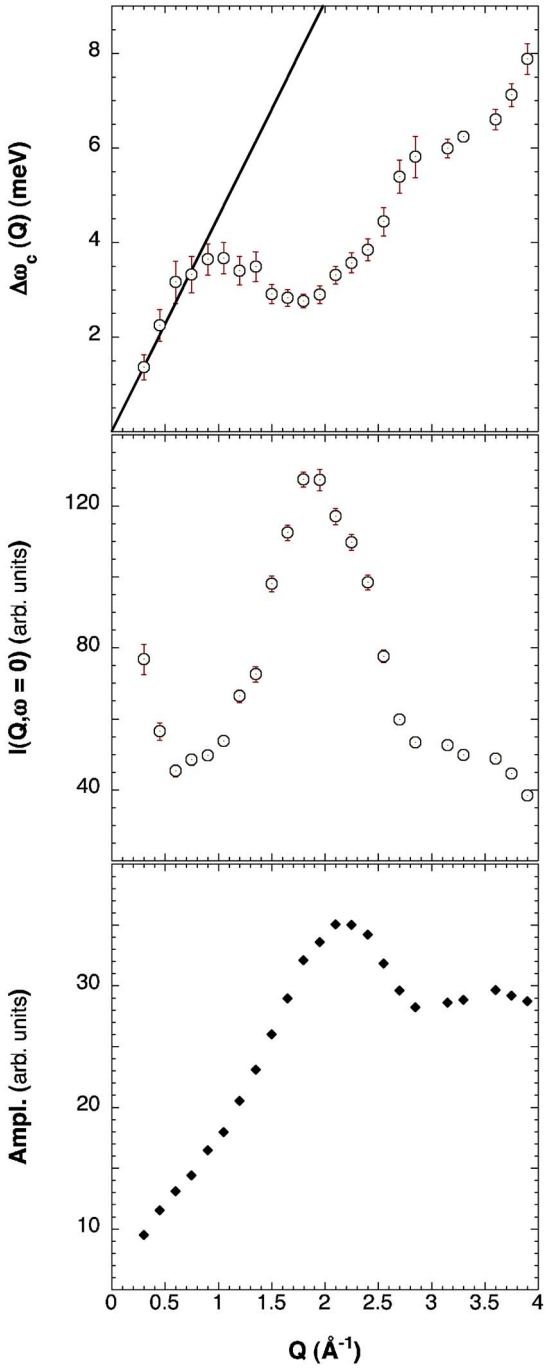

FIG. 3. (Color online) Spectral linewidths (top), peak intensities (middle), and integrated amplitudes (bottom) for the broad quasielastic component as measured on MARI at an incident energy of 14 meV. The straight line in the top panel depicts $\langle\omega_{\mathrm{ID}}^2\rangle^{1/2}$ for DF, the ideal-gas limit for the second spectral moment.

two Lorentzians, constraining the width of the narrower component to those obtained on IRIS and shown in Fig. 1(a). The model thus corresponds to that given by Eq. (1) and is able to account for the spectral line shapes within the explored range of momentum transfers. As shown in Fig. 3, this procedure yields estimates for the value of the linewidth of the broader component as well as Q-dependent peak heights and integrated amplitudes.

In Fig. 3, it can also be seen that the linewidth displays marked oscillations as well as a local minimum at Q_p. In turn, the peak intensity shows a well-defined maximum also at Q_p. These observations are sufficient to ascribe a mostly coherent character to such a feature, characterized by a Q-dependent linewidth $\Delta\omega_c$. The two lowest Q values might represent an exception to the earlier assignment since peak intensities show a significant increase for $Q<0.5$ Å^{-1}, with coherent and incoherent linewidths approaching similar values. As far as the nature of motions being sampled, Fig. 3 compares the derived linewidths to the ideal-gas limit characterized by a reduced second frequency moment $\langle\omega_{\mathrm{ID}}^2\rangle^{1/2} = \sqrt{2\ln 2(k_BT/M)}\cdot Q$. The slope of $\langle\omega_{\mathrm{ID}}^2\rangle^{1/2}$ versus Q corresponds to the thermal velocity of a free gas of particles of mass M and, thus, it is the asymptotic limit expected for a monatomic liquid as $Q\to\infty$. Our comparison clearly indicates that such a limit is well above the experimental data at high Q and renders further support to our assignment of these motions as arising from overdamped rototranslational motions, that is, molecular motions of diffusive or stochastic nature. In fact, the slope of $\langle\omega_{\mathrm{ID}}^2\rangle^{1/2}$ at high Q comes to be some 2.5 times larger than that of a free DF molecule which, translated into a change in particle mass, turns out to be 6–7 molecular units. On such grounds, we tentatively assign the observed coherent quasielastic scattering to that arising from short chains of bonded DF molecules characterized by a lifetime below 0.16 ps (4 meV). The fact that the slope of $\langle\omega_{\mathrm{ID}}^2\rangle^{1/2}$ at high Q values suggests a particle mass of 6–7 molecular units is fully consistent with experimental structural studies on liquid HF at the pair correlation level.[1] In this structural study, it was found that liquid HF is comprised of short chains which are on the average 6–7 molecules in length; specifically, each HF molecule forms ~0.86 hydrogen bonds per molecule. This finding is in opposition to the work of Ref. 7 where it is claimed that relaxation process in liquid HF may be determined by the number of hydrogen bonds per molecule when compared with water. However, Ref. 7 also assumes that each HF molecule forms exactly one hydrogen bond, which would result in a liquid structure that is comprised of infinite chains. While dynamical studies do not provide direct information regarding structure, they should be consistent with what is already known. Our present study is consistent with the average structure in the liquid while the former inelastic x-ray studies are not, as they do not account for the observation that HF molecules form less than one hydrogen bond per molecule. Infrared and Raman data of the stretching modes in HF and DF (Ref. 9) are also in line with our findings.

B. Inelastic scattering

Access to neutron energy transfers in the region of 10–20 meV also allows for a detailed assessment of the frequency range previously ascribed to purely propagating acoustic modes, as reported in Ref. 7. To this end, a somewhat higher incident neutron energy (E_0=40 meV) was employed while retaining an energy resolution of ΔE =0.76 meV, still below that used in Ref. 7 (ΔE=1.6 meV). In our case, knowledge of the coherent and incoherent quasielastic response in parametric form at smaller energy transfers (see previous section) serves the important purpose of

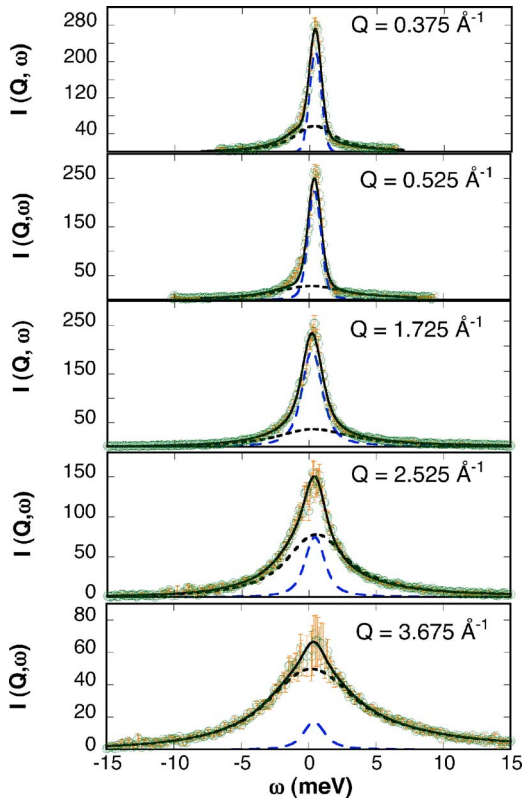

FIG. 4. (Color online) Inelastic spectra as a function of momentum transfer measured on MARI at E_0=40 meV. Model fits are shown in black while individual Lorentzian components in dashed black and blue.

constraining the spectral extent of these contributions. In other words, the procedure followed in the present work permits a reliable isolation of any additional spectral intensity appearing at this higher incident energy.

In molecular liquids, the presence of well-resolved features at finite frequencies can be unambiguously assigned to density oscillations (i.e., acoustic modes) provided that intensities from a different origin such as molecular reorientations or librational motions do not contribute significantly in the same spectral range.[20] Examples of such excitations are provided by the previously reported cases of liquid parahydrogen[21] or molten alumina,[22] where the presence of resolved features in the inelastic spectra can be followed by the naked eye. In contrast, most liquids examined so far show far less marked features such as, for example, weak shoulders in the leading and trailing edges of the quasielastic region. Analysis of spectral intensities in these cases is therefore limited to the use of some ad hoc function. In this context, recourse has been usually made to expressions taken from solid-state physics such as those representing harmonic (albeit damped) oscillatory motions supplemented by quasielastic components to account for the central part of the spectra. The appearance of well-resolved features obviously depends upon the values of the excitation frequency compared to the damping factor. Whenever the latter compares or exceeds the excitation frequency, the functional form of such a motion becomes identical to that of a broad Lorentzian centered at zero frequency. It is the purpose of this section to explore whether the current inelastic neutron data for liquid

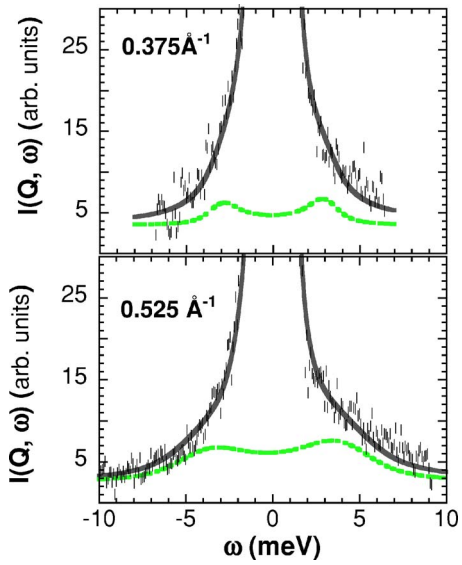

FIG. 5. (Color online) Experimental data (vertical bars) measured on MARI at T=203 K at an incident energy of 40 meV. A plausible DHO component in the inelastic spectrum is shown as a green dashed line. The total intensity (solid line) comprises two additional quasielastic (Lorentzian) contributions.

DF provide additional support for the presence of an underdamped collective mode as reported in Ref. 7.

A series of spectra measured on MARI at T=203 K is shown in Fig. 4. An estimate of the frequencies involved in sound propagation can be made by recourse to the values for the adiabatic and high-frequency sound velocities reported in Ref. 7. Extrapolation to T=203 K yields linear dispersion relations ω_0=4.47 Å meV and ω_∞=8.1 Å meV at zero and infinite frequency, respectively. Cursory inspection of Fig. 4 is sufficient to infer that these dispersion relations are not supported by our data, as there are no clearly identifiable features to be assigned to finite-frequency excitations within our energy- and momentum-transfer ranges. To further compare our results to those reported in Ref. 7, Fig. 5 displays spectra at two different momentum transfers where the inelastic contribution has been modeled with a putative damped harmonic oscillator (DHO)

$$I_{\mathrm{osc}}(Q,\ \omega) = Z(Q)\frac{4\omega\omega(Q)\Gamma(Q)}{[\omega^2 - \Omega(Q)^2]^2 + 4\omega^2\Gamma(Q)^2}. \qquad (3)$$

Neutron spectra were calculated using values for the oscillation frequency $\Omega(Q)=\sqrt{[\omega(Q)^2+\Gamma(Q)^2]}$ and damping terms $\Gamma(Q)$ given in Ref. 7. Only the oscillator strength $Z(Q)$ together with the linewidth and intensity of two additional quasielastic (Lorentzian) modes describing low-energy motions were left as free parameters. Attempts to optimize the value of the oscillator frequency and/or damping term did not lead to successful fits of the spectra.

The comparison of experimental and calculated spectra provided by Fig. 5 shows quite clearly that somewhat less than 10% of the total intensity can, at best, be ascribed to a well-defined inelastic mode. While the presence of such a relatively small component could be accounted for by a DHO-type model, the obtained values for the linewidths of both Lorentzians differed considerably from those we have derived from our higher-resolution measurements on IRIS

and MARI, as described in the previous section. In the present circumstances, Ockham's razor calls for a description of our data with fewer parameters than those required if a DHO was employed as fit function. To this end, a model comprised by three Lorentzians with the linewidths of the two narrower modes set to those obtained from our quasielastic measurements at lower energy transfers yields χ^2 values about one half lower than those obtained if a DHO description is chosen. On such grounds, we conclude that there is no compelling experimental evidence to support the notion of well-defined, finite-frequency excitations in liquid DF. Instead, inelastic neutron scattering data within the kinematic range explored by our experiments, that is, $Q>0.30$ Å^{-1} and energy transfers up to 20 meV are well accounted for in terms of a Lorentzian centered at zero frequency and characterized by a linewidth $\Delta\omega_{\mathrm{inel}}(Q)$ and line strength $I_{\mathrm{inel}}(Q,\ \omega=0)$. Because of the relatively large energy transfers involved, this spectral component may be tentatively assigned to overdamped collective modes rather than to processes involving stochastic molecular motions. The wave vector dependence of the linewidth and amplitude are shown in Fig. 6.

The data shown in Fig. 6 display a strong modulation of mode widths and amplitudes as a function of wave vector. As expected, the latter shows a maximum at Q_p together with a rise at low Q's indicative of an incoherent-scattering contribution still persisting at these relatively large momentum transfers. The linewidths shown in the upper frame of Fig. 6 are more than twice as large as those explored using the lower incident energy of 14 meV which were assigned to pure reorientational motions. In terms of characteristic times, the overdamped inelastic processes here sampled correspond to an average of 0.2 ps, whereas those involved in rotational motions are about one order of magnitude larger, especially at low momentum transfers ($Q<1$ Å^{-1}). Such values are to be referred to those characteristic of long-range translational diffusion which, for a temperature $T=203$ K and the lowest explored Q values, would yield times over 30–40 ps.

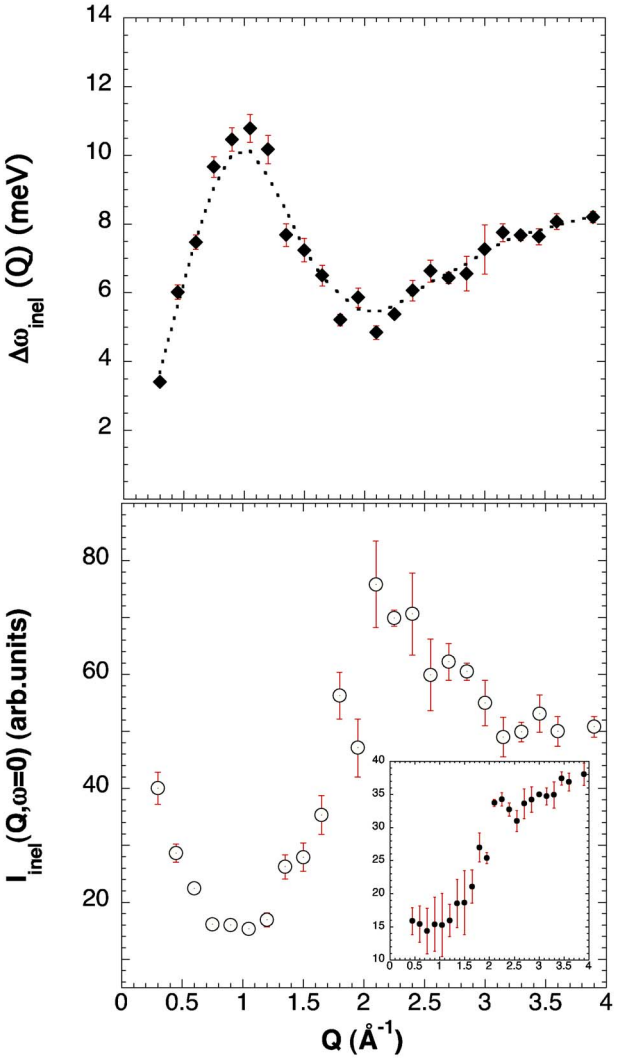

FIG. 6. (Color online) Spectral linewidths (top), amplitudes (bottom), and integrated intensities (inset, bottom) of the overdamped inelastic component as measured on MARI at an incident energy of 40 meV. Lines are drawn as guides to the eye.

IV. DISCUSSION AND CONCLUSIONS

The main finding of the present work is the presence of three well-defined time scales in liquid DF in addition to those of librational or opticlike nature explored in our previous work.[13] We ascribe these characteristic times to molecular center-of-mass motions, molecular rotations, and overdamped collective excitations, respectively. The striking difference in time scales between mass diffusion and reorientational motions had already been established in our previous report on single-particle dynamics in liquid HF.[14] The picture that emerged from this study portrayed rotational motions as being about one order of magnitude faster than translational motions. Moreover, stochastic rotations displayed a rather mild dependence with temperature. In other words, rotational motions in liquid HF are far less hindered by intermolecular interactions than what could be expected based on the strength of the hydrogen bond alone. The separation between translations and rotations is to be expected given the rather disparate masses of hydrogen and fluorine. This separation has also been seen in computer simulations.[10,12] Additionally, computer molecular dynamics investigations[12] have shown that the velocity autocorrelation function for center-of-mass motions displays a tail lasting for several picoseconds which is absent in the corresponding atomic correlation function for hydrogen. In juxtaposition with the HF molecule, hydrogen atoms only show noticeable oscillatory structure up to some 0.25 ps. Such long-lasting correlations in HF have, as an immediate counterpart, relatively high values for the self-diffusion coefficients, especially if compared to those of its nearly isobaric cousin, the water molecule. Specifically, self-diffusion in liquid HF takes place at a rate about three times faster than water in the same corresponding state. Thus, great care must be exercised when relating these two hydrogen-bonded fluids. At the macroscopic level, HF dynamic and kinematic viscosities are 4–5 times smaller than those of tetrahedrally coordinated water. Differences are even more dramatic at the atomic level as a linear HF molecule is characterized by a moment of inertia about ten times smaller than that of the highly asymmetric water molecule.[23]

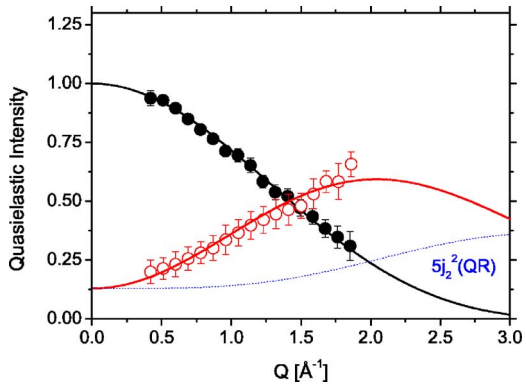

FIG. 7. (Color online) Wave vector dependence of the quasielastic form factors in liquid HF at $T=195$ K. Solid lines are fits to Eq. (4). The second term in the rotational cross section involving $j_2^2(QR)$ is also shown to illustrate the small contribution of higher-order ($l>1$) partial-wave terms over the explored Q range.

In light of these remarks, we can also consider data from our previous study on liquid HF.[14] There, it was found that quasielastic spectra down to temperatures just above the freezing point ($T=195$ K) conform to a model of isotropic rotational diffusion (deemed to be valid for weak hindering of molecular reorientations[24]), supplemented by a Q-independent background. To test how good these data are accounted for by such a model, we have taken the leading terms in the partial-wave expansion of the double-differential cross section and analyzed the intensities for the zeroth-order term (corresponding to pure translations) and the first two rotational terms (representative of reorientation of a vector of length $R=0.88$ Å joining the hydrogen nucleus to the molecular center of mass). Two adjustable scale factors A_{trans} and A_{rot} were left as free parameters. Mathematically, the model needed to analyze the quasielastic intensity $I_{\mathrm{qens}}(Q)$ reads

$$I_{\mathrm{qens}}(Q) = I_{\mathrm{trans}}(Q) + I_{\mathrm{rot}}(Q) + B,$$

$$I_{\mathrm{trans}}(Q) = A_{\mathrm{trans}} e^{-u^2Q^2/3} j_0^2(QR),$$

$$I_{\mathrm{rot}}(Q) = A_{\mathrm{rot}} e^{-u^2Q^2/3} [3j_1^2(QR) + 5j_2^2(QR) + \cdots], \qquad (4)$$

where the exponential term represents a Debye–Waller factor arising from fast vibrational motions and is given in terms of an isotropic mean particle displacement $u=0.47\pm0.04$ Å. The resulting fit using Eq. (4) is given in Fig. 7 and shows that both scale factors attain the same value within experimental error, that is $A_{\mathrm{rot}}/A_{\mathrm{trans}}=1.1\pm0.1$. As only a global, common scale factor is necessary to normalize translational and rotational intensities, it can be concluded that molecular motions within the liquid are very well represented in terms of infinitesimal reorientational displacements characterized by a rotational diffusion coefficient attaining values $\sim D_R = 0.38$ ps^{-1}. In turn, the background term amounts to a modest 10% of the total intensity.

Such a background arises from faster motions such as those executed by particles participating in collective motions. Given the nature of the intermolecular bonding in the liquid, these motions should correspond to particles hydrogen bonded to their neighbors; that is, the earlier result indicates that within our time window of 1–75 ps, ~90% of HF molecules are in a rather fluid state. One therefore expects that those taking part in chain or ring structures (where short chains comprise the average structure of the liquid[1,9] and shorter-lived structures are thought to involve up to 20 monomer units[10]), survive in such bonded states for times shorter than those covered by our temporal window. The present study is therefore consistent with a microscopic picture whereby hydrogen fluoride is in a highly fluid state down to its melting point, a result corroborated by measurements of diffusion coefficients by other techniques.[18] Moreover, most molecules execute weakly hindered motions. Such a finding also explains the absence of well-resolved features attributable to long-lived collective excitations since their lifetimes are deemed to be smaller than a small fraction of a picosecond. The reason for such a behavior appears to be related to the rather peculiar characteristics of the spectrum of generalized viscosity $\eta(Q,\omega)$ (Ref. 25) where, in contrast with the case for liquid water, a substantial portion of the spectral intensity is located at frequencies ~30 meV, corresponding to motions identified in our previous study.[13] These modes have a negligible contribution to this transport coefficient in the hydrodynamic limit.

In summary, our current results emphasize the striking differences in dynamic behavior shown by liquid HF if compared to the most investigated fluid, liquid water. Such differences also serve to accommodate the rather disparate values exhibited by the thermodynamic fixed points as well as by the macroscopic transport properties of both fluids. Furthermore, the distinct behavior of HF is also in line with results from diffraction studies[1] which portray the liquid as having a far sparser bonding structure than that characteristic of liquid water.

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